

Synthetic hydrate fuel, methane, gas

INTRODUCTION

Clathrates, particularly methane and other hydrocarbon gas hydrates, have been known as laboratory curiosities since chlorine hydrate ($\text{Cl}_2 \cdot 6\text{H}_2\text{O}$), was reported (Faraday, 1823). In the 1930's and 1940's the natural gas industry had problems with the formation of a crystalline, wax-like substance in natural gas transport pipes. This material clogged the lines and research was focused on understanding the origin and physical chemistry of the material so that its appearance in pipelines could be minimized. Methane hydrates are now recognized as being very widespread in marine sediments and in permafrost regions, and may constitute the largest store of fixed carbon on earth (Kvenvolden, 1993). Our present knowledge about methane hydrate physical chemistry, and the potential large volumes of recoverable methane from naturally occurring sources argues strongly that methane is likely to be the fuel of the future, especially if the aspect of compressing methane within a clathrate crystal lattice can be utilized on an industrial scale.

There is currently an increasing interest in methane as a fuel because the technology for handling it as a fuel, and the direct (e.g., on-site combustion for heating) and indirect (electricity generation) energy conversion technologies are well understood and cost effective. Additionally, because methane contains more hydrogen atoms for each carbon atom in its molecule than any other hydrocarbon fuel, less carbon dioxide is produced upon combustion. Also, gas field methane is usually relatively pure and relatively easy to purify. Its use as a fuel is thus more environmentally benign than other more complex hydrocarbon fuels or coal. Methane also produces much less carbon dioxide per mole than alcohols, where OH substitutes for one molecule of H, and much less than in liquid petroleum and oil based fuels.

Methane ("natural gas") produced from conventional gas deposits is plentiful, easily delivered (as a gas) to the user by an in-place domestic distribution system, and as a fuel, methane is clean burning and has a respectable heat content. The prospect of methane recovery from vast oceanic gas hydrate deposits, however, argues for an almost indefinite supply of methane, the recovery of which will probably speed the development of the gas-energy economy to replace the current oil-based economy. In addition to this development being ecologically sound, oil may be viewed better as an industrial feedstock than as a direct fuel, so long as a convenient, alternate source of energy such as methane is made available.

Methane is particularly amenable to transport and handling as a gas in pipelines and transport to point use in pipes within contiguous land areas. In fact, most of the early work into the chemistry of methane hydrates was undertaken by the gas transport industry because hydrates were forming and clogging gas pipelines even at relatively high temperatures and moderate pressures. Current technology frequently requires that methane fuel be moved as either compressed gas or as liquefied gas, as when natural gas is imported to the U.S. distribution grid from foreign gas fields. Of course, many fixed-site utilizations for natural gas (e.g. space heating, electrical power generation, or cooking) rely exclusively on gaseous methane as a fuel stock. Where technical or geographic difficulties prohibit the use of piped distribution, however, other means of distributing gas must be developed for use. Storage of methane (e.g., compressed gas) at the point of use may also be a problem so long as a continuous piped supply is not available.

Both compressed gas and liquefied gas, as transport media, possess serious safety concerns associated with the flammability of the material (compressed natural gas) or the cold temperatures and ultimate flammability/potentially explosive nature of the liquefied medium. This paper suggests and examines a new application of clathrate chemistry, which could have a significant impact on methane fuel use and distribution if implemented. We call attention to a potential third alternative for bulk gas transport and point-of-use storage, which would be energy dense, fairly stable, non-flammable in bulk, easy to transport, and potentially useable as-is for motor fuels.

SYNTHETIC METHANE CLATHRATE FUEL (SMCF)

Naturally occurring methane hydrates are not stable at sea level ambient temperatures and pressures. However, it is not intended to use pure methane hydrate as the basis for the new fuel transport and storage media. Current experimental results show that hydrates can be fabricated both from natural gas more dense than methane (de Boer et al, 1985) with variable physical property ranges that are stable well above the normal methane hydrate P-T stability field (Sloan, 1990). Also, in the course of producing synthetic methane hydrate, metastabilities about the liquidus line exist (Stern et al., 1996), which may point toward controlling metastability ranges of methane hydrate rather than expanding the methane hydrate stability field. This broader stability of naturally occurring multiple gas clathrates, poorly understood metastability, and relative ease with which synthetic methane (based) hydrate can be formed, leads us to suggest that research fabricating special property methane clathrates is feasible and that research should be undertaken to fabricate a new methane fuel storage and transport media.

The gas to be transported would be carried as a stabilized water-gas hydrate, or as a clathrate utilizing selected (probably gaseous) additives which could expand the stability field for pure methane-pure water clathrates well beyond that of natural methane hydrate or even some of the other natural hydrates that are stable nearer standard T-P (Fig. 1). It is clear that development and adoption of a clathrate-based fuel transportation/distribution system, to augment the in-place domestic gaseous-state fuel distribution complex, would offer many advantages above and beyond those associated with safety.

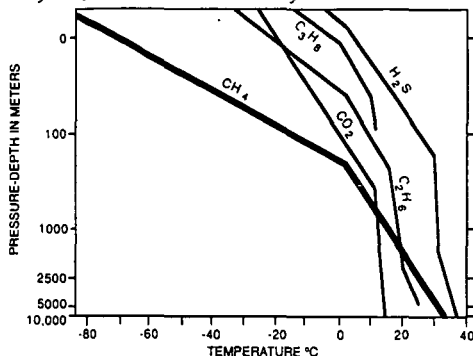


Figure 1. Natural hydrate phase boundaries for different common gases. From Makogon (1988). Replotted with temperature in normal scale and pressure-depth in meters seawater. 0 is atmospheric pressure at sea level. CH_4 , methane; C_2H_6 , ethane; C_3H_8 , propane; C_4H_{10} , butane, the highest molecular weight of the paraffin gases, which most easily forms clathrates. CO_2 , carbon dioxide; H_2S , hydrogen sulphide.

Although the energy density of methane clathrate is low compared with common liquid fuels (Table 1), its potential energy density is actually greater than a similar volume of liquid methane, and up to 164 times (Kvenvolden, 1993) the same volume of methane gas (at STP). The compression factor is obtained because methane molecules are forced closer together in the crystalline solid methane hydrate than is obtained by any other form of methane compression. For our energy conversion factor we use 160 X compression factor, although it is unlikely that the industrial synthetic fuel will actually have a compression factor that high, because it is conservatively less than the maximum anticipated and results in even numbers appropriate for preliminary estimation.

Fuel or form of methane	Formula	Density g/cc	Energy Content Btu/lb	Energy Content Btu/ft ³
Methane Gas	CH_4	7×10^{-4}	160 * ³	1,150 * ³
Methane Liquid	CH_4	0.42 * ²	1,500 * ⁴	152,000 * ⁴
Methane-water solid (natural hydrate energy conversion equivalent)	$\text{CH}_4(\text{H}_2\text{O})_6$	~ 1.0	277 * ⁴	15,800 * ⁴ * ⁵
Methane-water solid (natural hydrate potential)	$\text{CH}_4(\text{H}_2\text{O})_6$	~ 1.0	277 * ⁴	184,000 * ⁴ * ⁶
Octane (gasoline)	C_8H_{18}	0.70	19,000 * ³	840,000 * ³
JP-5 * ¹	$\text{C}_{14}\text{H}_{30}$	0.77	18,500 * ³	930,000 * ³

Table 1. Energy content of various Hydrocarbon Fuels. *¹, Less volatile jet fuel used by Navy, mandated for use on carriers to reduce danger of explosion. *², boiling point -161 C. *³, STP Conditions, gas phase. *⁴, Energy may be consumed producing gaseous methane from these forms or in containing them. *⁵, Combustion products are H_2O and CO_2 . Energy content takes into account energy required to decompose hydrate to H_2 and CH_4 ; this figure represents energy content after conversion at 150 volumes of methane in hydrate per

volume of methane at STP. *6. Total potential energy content with no account taken of dissociation energy requirements based on 160 volumes of methane in hydrate per 1 volume of methane at STP (engineering may reduce the energy requirements for dissociation from specially fabricated clathrate or natural heat sinks may be used as an energy source).

It must be pointed out that the precise nature of SMCF is not known because it has yet to be designed and fabricated. Thus, the energy density, energy losses upon fabrication and subsequent gasification, and the equivalent energy of methane after conversion, in addition to the cost of the conversion and other engineering necessary for an SMCF system need to be known before a commercial value can be placed on the SMCF media. The potential energy content of naturally occurring methane hydrate is high enough to allow for some system or usage diminution and still remain an attractive new fuel storage and transport media. Thus, if an energy efficient means for gasifying synthetic methane clathrate fuel (SMCF), can be found, it may prove to be a more efficient means of compressing methane than liquefaction.

Because it is unlikely that the energy density of a clathrate-based fuel media will ever significantly approach that of liquid petroleum fuels, the clathrate fuel is clearly not appropriate for all vehicles. For instance, vehicles with small volumes capacity for fuel storage, such as private motor vehicles and aircraft, where weight/volume is a major factor, are not likely end-point users. Larger platforms, however, such as ships and possibly high-speed trains which could be made environmentally benign (with respect to noise of energy generation and exhaust), might be possible end-users, especially when the other attributes of clathrate based fuel media, such as inhibiting uncontrolled fires and explosions in commercial applications and explosion damping and deflecting in military applications, are taken into consideration.

The proposed safer transport system utilizes gas hydrates (clathrates) which are physical associations of water ice and low molecular weight gas molecules (e.g. methane, ethane, propane or butane). These clathrates form spontaneously when water and a suitable low molecular weight gas (e.g. methane, carbon dioxide, hydrogen sulfide, chlorine) are mixed at suitable temperatures (generally low) and pressures (generally moderate). Indeed, the older literature contains many references to gas hydrates forming spontaneously in natural gas transmission pipelines, and often blocking them; this potential situation requires the drying of gas prior to pipeline transportation (DoE, 1987).

Research into the low pressure species has mainly concerned developing techniques that will allow for industrial capability to efficiently dissolve, or gasify hydrates. Where bonding interaction between guest and host molecules might be enhanced somewhat, gas that normally does not hydrate, such as hydrogen, may be bound into specially formulated hydrates. If host cavities were to be lined with groups having a high hydrogen bonding character, such as hydroxyl or amino groups, other factors, such as the solubility parameter of the host, would be of less importance. Increased hydrogen bonding power might also be induced by charging guest molecules prior to exposure to hydrate lattice, or through the use of magnetic field charging (moving the fuel in a field, pulsing a field, or moving a field with respect to the orientation of the hydrate). Release of gas could be induced through heating, lowering of pressure, or electronic stimulation that would produce effects similar to that of microwaving food (where the frequency of the microwave is specific to water molecules).

FUEL SYSTEM REQUIREMENTS

The proposed SMCF storage and transport system would consist of three separate components: (1) Formation Module, (2) Transport Vessels, and (3) Gas Separation Unit.

(1). Hydrate Formation Module (HFM). Methane hydrates are stable under moderate pressures, and low temperatures (Fig. 1). The HFM will consist of a pressure vessel into which are pumped stabilizer, water spray, and methane; the P-T conditions of formation are presently uncertain but may be different from those needed for stability of the special hydrate during storage. Recent research shows that the methane hydrate forms immediately upon mixing water with the gas, when the system is within the stability field of the clathrate (Peter Brewer, MBARI, pers. comm., November, 1996). Once the hydrate is formed, the material would be removed from the HFM, and transferred to the transport vessel for movement to point of use or distribution.

(2) Hydrate Transport Vessel (HTV). The HTV would consist of a insulated container which could contain the stable special hydrate at ambient to moderate pressures. The insulation would more than likely consist of plastic foam such as is used by the refrigeration industry; vacuum jackets would be avoided because of cost and safety concerns. The HTV could be fabricated in any desired shape, and might evolve to be conformal to the hull or some interior structural members of the platform using the stored gas as a fuel, for example, in the double hull space of a ship.

(3) Gas Separation Unit (GSU). The GSU could be integral to the HTV, or separate, as mandated by the ultimate use of the released fuel gas. The clathrates are unstable in the presence of elevated heat; the hydrate could be decomposed by direct heating (e.g. a clathrate slush would be transferred to a heated vessel: gas evolves from the slush and escapes for use, and the water

from the hydrate is discarded or retained for use in making more hydrate later). Alternatively, the hydrate slush could be sprayed with water, the heat in which would be sufficient to decompose the hydrate. In either case, the evolved gas would be routed to a device (e.g. engine) which could use the combustible gas as a fuel.

It must be noted that there is no inherent reason why the units listed above would necessarily be separate components. For example, the storage vessel could contain integral sub-sections which would allow both formation of and decomposition of the gas hydrate right in the HTV. Further, it is technically possible to design and build an internal combustion engine which would use hydrate as the only, or majority, fuel; such a system would be similar to water-injection technology as applied to internal combustion engines, as in some experimental fighter plane engines and race cars.

CONCLUSIONS AND DISCUSSION

We have considered the feasibility of forming gas hydrates on demand, the utility of doing so (safe transportation of methane as a fuel), and potential end uses of gas moved as a hydrate (decomposition into gas for combustion, or design of engines to operate on hydrate itself). It is appropriate to examine the effects of adding a clathrate-based fuel on the current energy economy of a developed society.

Where would the SMCF system be applied and how would it develop? These questions cannot be fully answered because: 1. the engineering possibilities have yet to be explored, 2. the effect on market forces cannot be assessed beyond observing that the technology and potential fuel handling systems largely exist or can be developed at low cost, and, 3. government regulations that would apply (but do not yet exist) could either inhibit or promote development of both the SMCF itself and a world gas economy.

In the broadest sense, a SMCF-based fuel economy would be akin to the system based on liquid hydrocarbons. Specially formulated clathrates would be transported in the form of slush in much the same way as present liquid hydrocarbons. Transportation in solid form could utilize much of the present container-handling equipment and facilities including much of the sea, rail, and road equipment already in existence. Production as slush (Najafi and Schaetzle, 1989) would also allow pumped distribution. Moreover, where safety concerns are paramount, the SMCF might be used because of could greatly enhance safety; even in the presence of open flames, methane is evolved slowly from hydrates through breakdown of the crystal structure. This means that all of the gas or liquid methane available as an explosive component in present conventional methane storage media can only be evolved at a rate at which it could feed a fire, but not an explosion without first collecting evolved gas. In addition, upon gas evolution, substantial quantities of water are also produced, whose presence could be engineered to inhibit accidental ignition attributes of the system.

A dedicated clathrate-based methane fuel economy, in existence and developing, would drive exploration and development to utilize the vast quantities of methane that are only now being recognized as present on the planet (Max and Lowrie, 1996). Current conservative estimates indicate that naturally occurring methane hydrates contain at least twice the amount of fixed carbon as do conventional methane, liquid hydrocarbons, and coal, combined, on Earth (Kvenvolden, 1993), and it is unlikely that this fuel source will remain untapped, especially if an SMCF system can be developed at a reasonable cost.

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